

## CLAIMS

What is claimed is:

1. A microfluidic device, comprising:
  - (a) at least one channel for conducting a fluid, said channel having an internal channel surface formed in a substrate;
  - (b) a first polymer attached to the channel surface through photoinitiated grafting of a first monomer to selected regions of the channel surface; and
  - (c) a porous polymer monolith, comprised of a second monomer, in said channel, and attached to said first polymer in the selected regions, wherein the first and second monomers may be the same or different.
2. The device of claim 1 wherein said substrate is thermoplastic and transparent to light in the wavelength range of 200 to 350 nm.
3. The device of claim 4 wherein the thermoplastic substrate is selected from the group consisting of poly(methyl methacrylate), poly(butyl methacrylate), poly(dimethylsiloxane), polyolefin, cyclic olefin copolymer, polyethylene, polypropylene, poly(ethylene terephthalate), poly(butylene terephthalate), polyimide and hydrogenated polystyrene.
4. The device of claim 1 wherein said thermoplastic substrate is a polyolefin.
5. The device of claim 4 wherein the thermoplastic substrate polyolefin is cyclic olefin copolymer.
6. The device of claim 1 wherein the substrate is selected from the group consisting of PS-H, COC and PP.
7. The device of claim 1 wherein the channel is 10-200  $\mu\text{m}$  deep.

8. The device of claim 1 wherein the first polymer attached to the channel surface for grafting is comprised of one or more monomers selected from the group consisting of a polyvinyl monomer, a monovinyl monomer, and a mixture of a polyvinyl and monovinyl monomer.

9. The device of claim 8 wherein said monovinyl monomer is selected from the group consisting of acrylic acids, methacrylic acids, acrylamides, methacrylamide alkyl derivatives of methacrylamide, alkyl derivatives of acrylamide, alkyl acrylates, alkyl methacrylates, perfluorinated alkyl acrylates, perfluorinated alkyl methacrylates, hydroxyalkyl acrylates and hydroxyalkyl methacrylates, wherein the alkyl group in each of the aforementioned alkyl monomers has 1-10 carbon atoms, oligoethyleneoxide acrylates, oligoethyleneoxide methacrylates, vinylazlactones, and acrylate and methacrylate derivatives including primary, secondary, tertiary, and quarternary amine functionalities and zwitterionic functionalities.

10. The device of claim 8 wherein said polyvinyl monomer is one or more monomers selected from the group consisting of alkylene diacrylates, alkyl dimethacrylates alkylene diacrylamides, alkylene dimethacrylamides, hydroxyalkylene diacrylates, hydroxyalkylene dimethacrylates, wherein the alkylene group in each of the aforementioned alkylene monomers consists of 1-6 carbon atoms, oligoethylene glycol diacrylates, oligoethylene glycol dimethacrylates, vinyl esters of polycarboxylic acids, divinyl ethers, pentaerythritol di-, tri-, or tetramethacrylates, pentaerythritol di-, tri-, or tetraacrylates, trimethylopropane trimethacrylates, trimethylopropane acrylates, alkylene bis acrylamides and alkylene methacrylamides.

11. The device of claim 1 wherein the first polymer attached to the channel surface for grafting is comprised of at least one monomer selected from the group consisting of AAm, BuA, AMPS, EDA, EDMA, MMA and MA.

12. The device of claim 1 wherein the porous polymer monolith is comprised of polymerized polyvinyl monomers or a mixture of polyvinyl and monovinyl monomers.

13. The device of claim 12 wherein the polyvinyl monomers for the monolith comprise one or more monomers selected from the group consisting of alkylene diacrylates, alkylene

dimethacrylates, hydroxyalkylene diacrylates, hydroxyalkylene dimethacrylates, alkylene bisacrylamides, alkylene bismethacrylamides, wherein the alkylene group each of the aforementioned alkylene monomers has 1-6 carbon atoms, oligoethylene glycol diacrylates, oligoethylene dimethacrylates, diallyl esters of polycarboxylic acids, divinyl ethers, pentaerythritol di-, tri-, or tetraacrylates, pentaerythritol di-, tri-, or tetra methacrylates, trimethylopropane triacrylates and trimethylopropane trimethacrylates.

14. The device of claim 12 wherein the monovinyl monomers for the monolith comprise a monomer selected from the group consisting of acrylic acids, methacrylic acids, acrylamides, methacrylamide alkyl derivatives of methacrylamide, alkyl derivatives of acrylamide, alkyl acrylates, alkyl methacrylates, perfluorinated alkyl acrylates, perfluorinated alkyl methacrylates, hydroxyalkyl acrylates and hydroxyalkyl methacrylates, wherein the alkyl group in each of the aforementioned alkyl monomers has 1-10 carbon atoms, oligoethyleneoxide acrylates, oligoethyleneoxide methacrylates, vinylazlactones, and acrylate and methacrylate derivatives including primary, secondary, tertiary, and quarternary amine functionalities and zwitterionic functionalities.

15. The device of claim 2 wherein the porous polymer monolith is comprised of a mixture of monomers selected from the group consisting of HEMA, EDMA and BuMA.

16. The device of claim 1 further comprising:

(d) a polymer chain having a functional group attached to a portion of the porous polymer monolith by photoinitiated grafting of a third monomer, wherein the first and second monomers may be the same or different and the third monomer is different from the second monomer.

17. The device of claim 16 wherein the third monomer bearing the functional group is selected from the group consisting of: acrylic acids, methacrylic acids, acrylamides, methacrylamides, alkyl acrylamides, alkyl methacrylamides, alkyl acrylates, alkyl methacrylates, perfluorinated alkyl acrylates, perfluorinated alkyl methacrylates, hydroxyalkyl acrylates, hydroxyalkyl methacrylates, wherein the alkyl group each of the aforementioned alkyl monomers has 1-10 carbon atoms, vinylazlactones, oligoethyleneoxide acrylates, oligoethyleneoxide methacrylates,

and acrylate and methacrylate derivatives wherein the derivatives comprise a primary, secondary, tertiary or quarternary amine or a zwitterion.

18. The device of claim 16 wherein the third monomer bearing the functional group is selected from the group consisting of: methyl acrylate, methyl methacrylate, butyl acrylate, butyl methacrylate, *tert*-butyl acrylate, *tert*-butyl methacrylate, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, acrylic acid, methacrylic acid, glycidyl acrylate, glycidyl methacrylate, 3-sulfopropyl acrylate, 3-sulfopropyl methacrylate, pentafluorophenyl acrylate, pentafluorophenyl methacrylate, 2,2,3,3,4,4,4-heptafluorobutyl acrylate, 2,2,3,3,4,4,4-heptafluorobutyl methacrylate, 1H,1H-perfluorooctyl acrylate, 1H,1H-perfluorooctyl methacrylate, acrylamide, methacrylamide, N-ethylacrylamide, N-isopropylacrylamide, N-[3-(dimethylamino)propyl] methacrylamide, 2-acrylamido-2-methyl-1-propanesulfonic acid, 2-acrylamidoglycolic acid, [2-(methacryloyloxy)ethyl]-trimethylammonium chloride, [2-(methacryloyloxy)ethyl]dimethyl(3-sulfopropyl)ammonium hydroxide, and 2-vinyl-4,4-dimethyl-azlactone.

19. The device of claim 16 wherein the third monomer is selected from the group consisting of AMPS, BuA and VAL.

20. A microfluidic device, comprising:

- (a) at least one channel for conducting a fluid, said channel having an internal channel surface formed in a substrate comprising a polyolefin;
- (b) a first polymer, comprised of a first polyvinyl monomer, attached to the channel surface through photoinitiated grafting of to selected regions of the channel surface; and
- (c) a porous polymer monolith, comprised of a second polyvinyl monomer, in said channel, and attached to said first polymer in the selected regions, wherein the first and second monomers may be the same or different.

21. The device of claim 20 further comprising:

(d) a polymer chain having a functional group attached to a portion of the porous polymer monolith by photoinitiated grafting of a third monomer, wherein the first and second monomers may be the same or different and the third monomer is different from the second monomer.

22. The device of claim 21 wherein the third monomer is an acrylate.

23. A method for preparing a microfluidic channel in a microfluidic device, comprising:

- (a) providing a substrate having at least one channel disposed thereupon;
- (b) filling the channel with a first monomer solution comprising a photoinitiator and a monomer;
- (c) exposing the solution to light for polymerizing said solution to a predetermined degree to form a polymer layer grafted to the wall of said channel;
- (d) removing ungrafted monomer from the channel;
- (e) filling the channel provided with the grafted polymer layer with a second monomer mixture including a photoinitiator for formation of a porous polymer monolith; and
- (f) exposing the second monomer mixture to light for polymerizing said second monomer mixture to form a porous polymer monolith attached to the wall of said channel through the grafted polymer layer.

24. The method of claim 23 wherein steps (b), (c) and (d) are repeated using different monomers to produce multiple grafted polymeric layers.

25. The method of claim 23 wherein the polymerization steps are achieved only in areas not restricted by a photomask.

26. The method of claim 23 wherein said substrate is a plastic transparent to light in the wavelength range of 200 to 350 nm.

27. The method of claim 26 wherein said substrate is selected from the group consisting of poly(methyl methacrylate), poly(butyl methacrylate), poly(dimethylsiloxane), polyolefin, cyclic

olefin copolymer, polyethylene, polypropylene, poly(ethylene terephthalate), poly(butylene terephthalate), polyimide, or hydrogenated polystyrene.

28. The method of claim 27 wherein said plastic is a polyolefin.

29. The method of claim 28 wherein the polyolefin is cyclic olefin copolymer.

30. The method of claim 23 wherein said monomer of said first monomer solution is a polyvinyl monomer, a monovinyl monomer or a mixture of a polyvinyl and monovinyl monomer.

31. The method of claim 30 wherein said monomer of said first monomer solution is selected from the group consisting of acrylic acids, methacrylic acids, acrylamides, methacrylamides, alkyl acrylamides, alkyl methacrylamides, alkyl acrylates and methacrylates, perfluorinated alkyl acrylates and perfluorinated alkyl methacrylates, hydroxyalkyl acrylates, hydroxyalkyl methacrylates, wherein each of the aforementioned alkyl groups has 1-10 carbon atoms, vinylazlactones, oligoethyleneoxide acrylates, oligoethyleneoxide methacrylates, and acrylate and methacrylate derivatives wherein the derivatives comprise a primary, secondary, tertiary or quaternary amine or a zwitterion.

32. The method of claim 30 wherein said polyvinyl monomer of said first monomer solution is selected from the group consisting of alkylene dimethacrylates, alkylene diacrylamides, alkylene dimethacrylamides, hydroxyalkylene dimethacrylates, hydroxyalkylene diacrylates, wherein each of the aforementioned alkylene groups has 1-6 carbon atoms, oligoethylene glycol dimethacrylates, oligoethylene glycol diacrylates, vinyl esters of polycarboxylic acids, divinyl ethers, pentaerythritol di-, tri-, or tetramethacrylates, pentaerythritol di-, tri-, or tetraacrylates, trimethylpropane trimethacrylates, trimethylpropane triacrylates, alkylene bisacrylamides, alkylene methacrylamides, and mixtures thereof.

33. The method of claim 23 wherein said photoinitiator is an aromatic ketone.

34. The method of claim 33 wherein said photoinitiator is selected from the group consisting of benzophenone, 2,2-dimethoxy-2-phenylacetophenone, dimethoxyacetophenone, xanthone, thioxanthone, their derivatives, and mixtures thereof.

35. The method of claim 23 further comprising the step of adding said first monomer solution to a solvent that does not absorb UV light.

36. The method of claim 35 wherein said solvent is selected from the group consisting of water, alcohols and mixtures thereof.

37. The method of claim 36 wherein said alcohol is selected from the group consisting of butyl alcohol, dodecanol, isopropanol, pentanol and cyclohexanol.

38. The method of claim 23 wherein said exposing to light comprises using a photomask.

39. The method of claim 38 wherein said second monomer mixture for formation of a porous polymer monolith is comprised of a polymerized monovinyl monomer or a polymerized mixture of a polyvinyl and monovinyl monomer.

40. The method of claim 39 wherein said monovinyl monomer of said second monomer mixture is selected from the group consisting of acrylic acids, methacrylic acids, acrylamides, methacrylamides, alkyl acrylamides, alkyl methacrylamides, alkyl acrylates, alkyl methacrylates, perfluorinated alkyl acrylates, perfluorinated alkyl methacrylates, hydroxyalkyl acrylates, hydroxyalkyl methacrylates, wherein each of the aforementioned alkyl groups has 1-10 carbon atoms, vinylazlactone, oligoethyleneoxide acrylates, oligoethyleneoxide methacrylates, and acrylate and methacrylate derivatives wherein the derivatives comprise a primary, secondary, tertiary, or quarternary amine or a zwitterion.

41. The method of claim 39 wherein said polyvinyl monomer of said second monomer mixture is selected from the group consisting of alkylene dimethacrylates, alkylene diacrylamides, alkylene dimethacrylamides, hydroxyalkylene dimethacrylates, hydroxyalkylene diacrylates, wherein

each of the aforementioned alkylene groups has 1-6 carbon atoms, oligoethylene glycol dimethacrylates, oligoethylene glycol diacrylates, vinyl esters of polycarboxylic acids, divinyl ethers, pentaerythritol di-, tri-, or tetramethacrylates, pentaerythritol di-, tri-, or tetraacrylates, trimethylopropane trimethacrylates, trimethylopropane triacrylates, alkylene bisacrylamides, alkylene methacrylamides, and mixtures thereof.

42. The method of claim 39 wherein the second monomer mixture further comprises a surfactant.

43. The method of claim 23 further comprising the step of:

(g) contacting the polymerized porous monolith with a third monomer containing a functional group and grafting the monomer to the monolith by photoinitiated polymerization.

44. The method of claim 43 wherein said third monomer further comprises a solvent.

45. The method of claim 43 wherein said third monomer containing a functional group comprises a functional group selected from the group consisting of hydrophilic, hydrophobic, ionizable, and reactive functionalities.

46. The method of claim 45 wherein said third monomer containing a functional group is selected from the group consisting of methyl acrylate, methyl methacrylate, 2-acrylamido-2-methyl-1-propanesulfonic acid, butyl acrylate, butyl methacrylate, *tert*-butyl acrylate, *tert*-butyl methacrylate, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, acrylic acid, methacrylic acid, glycidyl acrylate, glycidyl methacrylate, ethylene diacrylate, ethylene dimethacrylate, 3-sulfopropyl acrylate, 3-sulfopropyl methacrylate, pentafluorophenyl acrylate, pentafluorophenyl methacrylate, 2,2,3,3,4,4,4-heptafluorobutyl acrylate, 2,2,3,3,4,4,4-heptafluorobutyl methacrylate, 1H,1H-perfluorooctyl acrylate, 1H,1H-perfluorooctyl methacrylate, acrylamide, methacrylamide, *N*-isopropylacrylamide, potassium salt and (2-acrylamido-2-methyl-1-propanesulfonic acid, 2-acrylamidoglycolic acid monohydrate, *N*-[3-(dimethylamino)propyl] methacrylamide, *N*-ethylacrylamide, [2-(methacryloyloxy)ethyl]-trimethylammonium chloride, 1,1,1,3,3,3-hexafluoro-2-propanol, potassium salt and [2-(methacryloyloxy)ethyl]dimethyl(3-sulfopropyl)ammonium hydroxide, inner salt and 4,4-dimethyl-2-vinylazlactone.